PATENT SPECIFICATION

(11) 1 318 442

NO DRAWINGS

(19)

1 318 442

(21) Application No. 41127/70 (22) Filed 26 Aug. 1970
(31) Convention Application No. 6 931 209 (32) Filed 12 Sept. 1969 in
(33) France (FR)
(44) Complete Specification published 31 May 1973
(51) International Classification C01F 7/02
(52) Index at acceptance C1A N4B

(54) METHOD OF MANUFACTURING ELECTRICALLY FUSED REFRACTORY PRODUCTS OF ALUMINA WITH A HIGH CORUNDUM CONTENT, AND PRODUCTS OBTAINED THEREBY

(71) We, L'ELECTRO-REFRACTAIRE, a French Body Corporate, of 39, Rue Cambon, 75-Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of manufacturing electrically fused refractory products of alumina with a high corundum content, which are compact, free from impurities, and have a low cost price.

French Patent Specification No. 1,208,577 and its additions Nos. 75,893, 82,057, 82,310 and 84,155 state that the majority of defects in products based on refractory oxides result from the reducing action exerted on the molten bath when the fusion is effected in the electric arc under resistor conditions — i.e. with the graphite electrodes immersed in the bath, or under short arc conditions — i.e. with the graphite electrodes arranged just above the bath. Indeed, resistor operation exerts a reducing action because the particles of graphite torn from the electrodes by the arc mix with the bath, reducing certain impurities present in the raw materials of the charge, such as the oxides of iron, silicon, phosphorous, sulphur, and causing a deficiency of oxygen. Short arc operation also exerts a slightly reducing action because the particles of graphite torn from the electrodes by the arc are not completely burnt before reaching the bath. The products obtained in this way contain metallic impurities, carbon, suboxides etc., which affect the properties of the products.

The above French Patent Specification, and its additions, recommend that these disadvantages be overcome by performing the fusion under long arc condition — i.e. with the graphite electrodes arranged well above the bath, which enables the particles of graphite torn away by the arc to be burnt before coming into contact with the bath when operating under normal conditions, in which air is present above the bath. They also propose bubbling or oxidising or neutral gas into the molten bath in order to agitate it and thus enhance the oxidising action of the fusion upon the molten bath.

Experience has shown that the long arc fusion method is a very satisfactory method for manufacturing compact alumina products, provided their corundum content is not too high (below 75%), but that if an increase in the corundum content is required, the adjustments of the long arc become increasingly critical and the results uncertain. The method is then no longer industrially viable.

In addition, French Patent Specification No. 1 429 550 discloses a method of manufacturing molten and cast refractory products with a high content of alpha-alumina, the principal feature of which consists in adding a small quantity of lithium carbonate to the charge and in performing a fusion preferably under conditions which avoid introducing carbon into the bath (long arc operation). The addition of lithium carbonate permits the adjustment of the arc to be rendered less highly critical. However, this method has the disadvantage of being expensive.

Furthermore, Hungarian Patent Specification No. 152 204 discloses a method of manuturing very finely crystallised corundum products, according to which air or oxygen is blown into the mass molten in the electric arc so as to oxidise the impurities such as carbon, which are dispersed in the mass. This method is rather delicate to perform and does not yield a regular product, since the quantity of oxidisable impurities (especially carbon) is very variable from one melting operation to the next, and the excess oxygen used can produce a certain porosity which is detrimental to the quality of the

products.

Lastly, U.S.A. Patent Specification No. 2 196 075 discloses that it is possible to prepare compact products containing alumina as the principal constituent by suitably regulating the degree of reduction or oxidisation of the alumina. To this end, the said Patent recommends adding to the molten mass, small quantities of carbon and of a reducible substance chosen from bauxite, rutile and ferric oxide, until a suitable redox equilibrium is reached by trial and error. Indeed, according to this Patent, the carbon reduces the porosity of the product, but must not be present in too great a quantity, which would be detrimental to the properties of the final product. This method has the disadvantage of introducing into the final product impurities which are always detrimental to its properties.

Thus, all the prior art methods suffer from various disadvantages for the manufacture of alumina products with a high corundum content: excessively unstable and critical adjustment (method of French Patent 1 208 577 and its additions), cost price of product too high (method of French Patent 1 429 550), addition of undesirable impurities (method of U.S.A. Patent 2 196 075) or impossibility of obtaining a constant quality (method of Hungarian Patent 152 204).

The subject of the present invention is an improved method of manufacturing alumina products with a high corundum content which is free from these disadvantages and permits of obtaining in a reproducible manner, compact and cheap products, it being clearly understood that by "products with a high corundum content" we are referring to those with a corundum content of between 75 and 98% by weight.

According to this invention there is provided a method of manufacturing a compact alumina product containing from 75 to 98% by weight of corundum, which comprises (a) melting an alumina-based batch containing less than 0.1% of Fe_2O_3, less than 0.1% of TiO_2, and the batch containing an amount of alkali metal compounds and optionally alkaline earth metal compounds lower than that which would prevent the obtention of at least 75% by weight of corundum, in an electric arc furnace operating under so-called short arc conditions, (b) adding in said batch or into the molten material obtained in step (a) an amount of a solid reducing agent sufficient for reducing those impurities present in the batch which are capable of being reduced, said solid reducing agent introducing no material which will detrimentally affect the final product, then (c) blowing into the molten material an amount of an oxidising gas sufficient to bring said molten material just to the oxidation-reduction equilibrium, and, finally, (d) rapidly casting the molten material after the step (c).

The term "alumina based batch" as employed in this description, embraces not only charges of pure alumina — i.e. alumina containing only minimal quantities (less than 0.1%) of Fe_2O_3 and TiO_2, but charges also of alumina containing certain desired additions, for example compounds of alkali and alkaline earth metals intended to influence the nature of the residual phases other than corundum, or B_2O_3 to enable the Na_2O content of the alumina used to be reduced.

In order to obtain a consistent quality of the product, it is essential that the successive reduction and oxidation should take place under reproducible conditions.

In order to obtain satisfactory reproducibility of the reduction, the fusion is performed, as stated, in the electric arc under short arc conditions so that the quantity of graphite coming from the electrodes and falling into the bath is minimal and as constant as possible from one fusion operation to the next and a pre-determined quantity of a reducing agent is added deliberately, sufficient to reduce the oxidizable impurities present in this batch and to permit subsequent degassing of the latter, so as to obtain non-porous products. It should be observed that "resistor fusion" would not be suitable because baths of molten alumina attack graphite electrodes in a highly irregular manner, so that the quantity of graphite coming from the electrodes is highly variable from one fusion to the next, and would not permit reproducible reduction conditions to be obtained.

The quantity of reducing agent to be added depends on the content of oxidisable impurities in the alumina charge. Where carbon or graphite is used as reducing agent, it has been found that a proportion of approximately 0.5% of the reducing agent referred to the weight of the charge is generally satisfactory.

The use of carbon or graphite as reducing agent is preferred because the carbon or graphite is afterwards eliminated from the bath during the oxidation stage in the form of CO. It is also possible to use as reducing agent aluminium or aluminium carbide, which upon oxidation will yield alumina which will not pollute the molten bath.

Any oxidising gas may be used for the oxidation. However, carbon dioxide, which decomposes at high temperatures into carbon monoxide and oxygen gives the most reproducible results. Obviously oxygen can also be used.

The quantity of oxidising gas to be blown into the bath of course, varies according to the size of the charge, the nature of the raw materials forming that charge, and with

the quantity of reducing agent introduced into the bath by deliberate addition and by being torn from the electrodes. The said quantity of oxidising gas is, therefore, determined experimentally by removing ladles of the fused material while the oxidising gas is being blown.

The following can be observed from the sample ladles: (a) the presence or absence of dissolved gases in the molten bath. For if the molten material contains little or no dissolved gases, a shrinkage cavity or pipe rapidly occurs and causes the liquid to separate from the top crust which develops, due to cooling by radiation, before this crust covers the entire free surface of the ladle, so that the formation of a hole in that surface is observed and generally a pipe cavity with bridges descending more or less helicoidally into the interior of the ladle, is to be seen. By contrast, if the molten liquid contains dissolved gases it has a tendency to rise outwards under the pressure of the gases which are liberated during solidification. In this case no rapid separation occurs between the liquid and the top crust, consequently the latter occupies the total free surface of the ladle and has no hole. The internal pipe which forms also has tight horizontal bridges which have developed subsequently in the same manner as the top crust; (b) the redox state of the solidified product of the ladle. For the oxidised products are perfectly white whereas the reduced products are grey to black. It should also be observed that excessively oxidised products (very white and with fine crystallisation) or insufficiently oxidised products (blackish to black) are not compact and contain bubbles.

For the purpose of the present invention, it is considered that the bath is sufficiently oxidised and that the redox equilibrium has been reached when the ladle has a hole in its upper part (rapid pipe formation, hence liquid containing little or no dissolved gases) and is of a slightly marbled white colour.

So long as the redox equilibrium has not been reached (product in the reduced state), the contents of the ladles are without a hole and are of a black colour. Likewise, if the oxidisation has been excessive and equilibrium has been passed, no hole is observed at the surface of the contents of the ladle either, and the latter is perfectly white.

It clearly appears that pure alumina products in the molten state dissolve gases very easily (irrespectively of the fusion procedure employed), but that these gases can be eliminated by a reduction of the molten bath, making degassing possible, followed by an oxidising blowing which stirs the bath and eliminates the dissolved gases, whilst oxidising the reduced impurities which are prejudicial to the quality of the final product.

However, care must be taken to stop the said oxidising blowing as soon as the redox equilibrium is reached, since from that moment onwards the blowing gases would in turn be dissolved in the bath. It is also necessary to cast the molten bath rapidly after this equilibrium has been reached, since it would then be capable of redissolving the atmospheric gases (air) present above the bath.

These phenomena are important, since they enable the present method to be distinguished from the method of the U.S.A. Patent No. 2 196 075 according to which it is possible by adding oxidising or reducing products, to work round the redox equilibrium, and wherein a reversible equilibrium, without dissolution of gases is observed, this fact being probably due to the presence of impurities (Fe_2O_3, TiO_2, bauxite etc.) in the bath which also affects the properties of the final product.

It should be observed that the experimental determination of the quantity of oxidising gas to be blown need be carried out only for the melting of the first charge, provided that the operative conditions for the subsequent melting remain unchanged (raw materials, short arc adjustment, quantity of reducing agent added).

Preferably, the blowing of the oxidising gas is performed with the current switched off in order to reduce as far as possible the dissolution of gases in the bath by stirring the latter, after the redox equilibrium is reached. The oxidising gas may be blown by means of a water cooled copper tube which is immersed in the molten bath at the time of the operation. This tube is of a similar type to those currently used in oxygen converters for steel production.

The following non-limitative examples are given in order to illustrate the invention.

EXAMPLE 1. To a charge of alumina containing Na_2CO_3 in a proportion corresponding to 0.65% by weight of Na_2O, graphite powder was added at the rate of 0.5% of the weight of the said charge. The whole was melted in the electric arc operating with a short arc of 0.5 to one cm, and a potential of 165 volts and an intensity of 5800 amperes, then CO_2 was blown into the bath. The quantity of CO_2 used was 2100 normal litres per ton of charge. By casting the material thus obtained, blocks of alumina were obtained comprising approximately 90% of corundum, which were white to pale grey, compact (density above 3.55 gm/cm^3; generally of the order of 3.70 gm/cm^3) and coarsely crystalline.

EXAMPLE 2. The procedure of Example 1 was followed, except that the blowing of CO_2 was replaced by a blowing of 1900

normal litres of oxygen per ton of charge. The blocks produced by casting the material thus obtained was similar to those of Example 1, except that they showed finer crystallisation.

EXAMPLE 3. The procedure of Example 1 was followed, except that the charge also contained 0.60% by weight Li_2CO_3 as ionising agent intended to increase the stability of the electric arc, and the quantity of CO_2 blown was 2500 normal litres per ton of charge. The blocks produced by casting the material thus obtained were similar to those of Example 1.

EXAMPLE 4. The procedure of Example 3 was adopted, except that the blowing of CO_2 was replaced by blowing of 1400 normal litres of oxygen per ton of charge. The blocks produced by casting the material thus obtained were similar to those of Example 2.

EXAMPLE 5. To a charge of alumina containing 2.50% by weight of magnesia, 0.5% of Na_2O, 1% by weight of B_2O_3, graphite powder was added at the rate of 0.6% by weight of the said charge. The whole was melted in the electric arc, operating with a short arc of 1 - 2 cm, at a potential of 165 volts and an intensity of 5800 amperes, then CO_2 was blown into the molten bath. The quantity of CO_2 used was 2600 normal litres per ton of charge. By casting the material thus obtained, blocks of alumina were produced comprising approximately 95% of corundum plus spinel, which were grey-pink in colour and compact - density in gr/cm^3 = 3.60 to 3.70.

EXAMPLE 6. The procedure of Example 5 was followed, except that the blowing of CO_2 was replaced by a blowing of 1500 normal litres of oxygen per ton of charge. The blocks produced by casting this material thus obtained was similar to those of Example 5.

EXAMPLE 7. A charge consisting by weight of 97% of alumina containing 0.55% of Na_2O, 1% of CaF_2 and 1.5% of CaO together with 0.5% of graphite, was melted in the electric arc operating with a short arc, at a potential of 175 Volts and at an intensity of 5800 amperes, then oxygen was blown 1800 normal litres per ton of charge. By casting the material thus obtained, blocks of alumina were produced comprising approximately 85% of corundum and having a density in gr/cm^3 of 3.60 to 3.75.

EXAMPLE 8. A charge consisting by weight of 96.9% of alumina containing 0.55% of Na_2O, 2.3% of CaO and 0.3% of B_2O_3 together with 0.5% of powdered graphite, was melted in the electric arc, operating with a short arc, at a potential of 175 Volts and at an intensity of 5800 amperes, then oxygen was blown into the molten bath. The quantity of oxygen blown into the bath was 2300 normal litres per ton of charge. By casting the material thus obtained blocks of alumina were produced comprising approximately 86% of corundum and having a density in gr/cm^3 of 3.60 to 3.75.

1. A method of manufacturing a compact alumina product containing from 75 to 98% by weight of corundum, which comprises (a) melting an alumina-based batch containing less than 0.1% of Fe_2O_3, less than 0.1% of TiO_2, and the batch containing an amount of alkali metal compounds and optionally alkaline earth metal compounds lower than that which would prevent the obtention of at least 75% by weight of corundum, in an electric arc furnace operating under so-called short arc conditions, (b) adding in said batch or into the molten material obtained in step (a) an amount of a solid reducing agent sufficient for reducing those impurities present in the batch which are capable of being reduced, said solid reducing agent introducing no material which will detrimentally affect the final product, then (c) blowing into the molten material an amount of an oxidizing gas sufficient to bring said molten material just to the oxidation-reduction equilibrium and, finally, (d) rapidly casting the molten material after step (c).

2. A Method according to Claim 1 characterised in that the oxidising gas is blown into the molten bath after switching off the current of the electric arc.

3. A Method according to Claim 1, characterised in that the reducing agent is constituted by carbon, graphite, aluminium or aluminium carbide.

4. A Method according to Claim 3, characterised in that approximately 0.5% of graphite powder is added referred to the weight of the charge.

5. A Method according to Claim 1, characterised in that the oxidising gas is carbon dioxide or oxygen.

6. A Method of manufacturing a compact alumina product containing from 75 to 98% by weight of corundum, substantially as described in any one of the Examples herein given.

7. The compact alumina products containing from 75 to 98% by weight of corundum obtained by means of a method according to any one of Claims 1 to 5.

HYDE, HEIDE & O'DONNELL,
47, Victoria Street,
London, S.W.1.
Chartered Patent Agents,
Agents for Applicants.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1973.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.